PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Commissioner
US Department of Commerce
United States Patent and Trademark Office, PCT
2011 South Clark Place Room CP2/5C24
Arlington, VA 22202
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 19 June 2001 (19.06.01)	
International application No. PCT/EP00/09196	**Applicant's or agent's file reference** 82585
International filing date (day/month/year) 19 September 2000 (19.09.00)	**Priority date** (day/month/year) 30 September 1999 (30.09.99)
Applicant IEZZI, Rodolfo et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

26 January 2001 (26.01.01)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

Th International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland**	Authorized officer Olivia TEFY
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
82585		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP00/09196	19/09/2000	30/09/1999
International Patent Classification (IPC) or national classification and IPC C07C15/46		
Applicant SNAMPROGETTI S.P.A et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 13 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
26/01/2001	19.12.2001
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Grammenoudi, S Telephone No. +49 89 2399 8324

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP00/09196

I. Basis f the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:
Description, pages:

1,2,4,6,8,9,11-14, 19-25	as originally filed			
3,5,7,10,15-18, 26-28	as received on	10/10/2001	with letter of	08/10/2001

Claims, No.:

2 (part),3-15, 16 (part)	as originally filed			
1,2 (part),16 (part), 17,18	as received on	10/10/2001	with letter of	08/10/2001

Drawings, sheets:

1/1	as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
   ☐ the language of publication of the international application (under Rule 48.3(b)).
   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.
   ☐ filed together with the international application in computer readable form.
   ☐ furnished subsequently to this Authority in written form.
   ☐ furnished subsequently to this Authority in computer readable form.
   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-18
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-18
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-18
	No:	Claims	

2. Citations and explanations
see separate sheet

D1= EP-A-0 905 112 & US-A-6 031 143

SECTION V

1. The present application pertains to a process for the production of styrene by dehydrogenating ethylbenzene.

2. Document D1 cited in the description on page 10 is considered to represent the closest state of the art. It discloses a process for the dehydrogenation of ethylbenzene to styrene which comprises all the features of present claim 1 except iron oxide as a component of the catalyst systems employed. D1 mentions two catalyst systems to be used, the one comprising Ga_2O_3, Pt, an alkaline and/or earth-alkaline oxide, silica and alumina, the other consisting of Cr_2O_3, SnO, an alkaline oxide, silica and alumina (see D1, claims 5 and 6). The problem to be solved by the present application with respect to D1 is to provide an alternative process for dehydrogenating ethylbenzene to styrene.

3. The available prior art does not contain any suggestion which would have motivated the skilled person to selectively replace gallium oxide and platinum or chromium oxide in the catalyst systems used in D1 by iron oxide.
Accordingly, the subject-matter of claim 1 meets the requirements of Articles 33(2) and 33(3) PCT.

4. Dependent claims 2-18 concern particular embodiment of claim 1. They fulfil the requirements of Art. 33(2) and 33(3) PCT as well.

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

DE GREGORI, Antonella
Ing. Barzanò & Zanardo Milano S.p.A
Via Borgonuovo, 10
Milan
ITALIE

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing *(day/month/year)*	19.12.2001
Applicant's or agent's file reference: 82585	**IMPORTANT NOTIFICATION**

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP00/09196	19/09/2000	30/09/1999

Applicant
SNAMPROGETTI S.P.A et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/	Authorized officer
European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Pfitzner, G Tel.+49 89 2399-8032

Form PCT/IPEA/416 (July 1992)

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION**	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
82585		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/EP 00/ 09196	19/09/2000	30/09/1999
Applicant		
SNAMPROGETTI S.P.A		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readble form.

   [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. _____

   [ ] as suggested by the applicant.

   [ ] *because the applicant failed to suggest a figure.*

   [ ] because this figure better characterizes the invention.

   [X] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/[redacted]00/09196

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C15/46 C07C5/333 B01J23/78 B01J23/94

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 794 004 A (MONTECATINI TECNOLOGIE) 10 September 1997 (1997-09-10) claims	1
A	EP 0 905 112 A (SNAMPROGETTI) 31 March 1999 (1999-03-31) claims	16-18
P,A	& US 6 031 143 A (BUONOMO ET AL) 29 February 2000 (2000-02-29) cited in the application	
A	US 3 472 794 A (CARTER JAMES L ET AL) 14 October 1969 (1969-10-14) claims	7
A	AU 499 659 B (DOW CHEMICAL CO) 26 April 1979 (1979-04-26)	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 December 2000	02/01/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Van Geyt, J

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/[redacted]00/09196

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 0794004	A	10-09-1997	IT	MI960447 A	08-09-1997
			AU	716285 B	24-02-2000
			AU	1510397 A	11-09-1997
			BR	9701231 A	25-08-1998
			CA	2199218 A	08-09-1997
			CZ	9700650 A	17-09-1997
			HR	970129 A	30-04-1998
			HU	9700554 A	02-03-1998
			JP	10000359 A	06-01-1998
			NO	971062 A	09-09-1997
			PL	318846 A	15-09-1997
			SK	30497 A	10-09-1997
EP 905112	A	31-03-1999	IT	MI972175 A	26-03-1999
			CA	2246086 A	26-03-1999
			US	6031143 A	29-02-2000
US 3472794	A	14-10-1969	BE	737826 A	23-02-1970
			NL	6912378 A	16-02-1971
AU 499659	B	26-04-1979	AU	8426075 A	03-03-1977

WO 01/23336
PCT/EP00/09196

PAT T COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

To:
DE GREGORI, Antonella
Ing. Barzanò & Zanardo Milano
S.p.A.
Via Borgonuovo, 10
Milan
ITALIE

Date of mailing (day/month/year) 05 April 2001 (05.04.01)	
Applicant's or agent's file reference 82585	**IMPORTANT NOTICE**

International application No.	**International filing date** (day/month/year)	**Priority date** (day/month/year)
PCT/EP00/09196	19 September 2000 (19.09.00)	30 September 1999 (30.09.99)

Applicant
SNAMPROGETTI S.P.A. et al

1. *Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application* to the following designated Offices on the date indicated above as the date of mailing of this Notice:
   AU,KP,KR,US

   In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:
   AE,AG,AL,AM,AP,AT,AZ,BA,BB,BG,BR,BY,BZ,CA,CH,CN,CR,CU,CZ,DE,DK,DM,DZ,EA,EE,EP,ES,
   FI,GB,GD,GE,GH,GM,HR,HU,ID,IL,IN,IS,JP,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MA,MD,MG,MK,
   MN,MW,MX,MZ,NO,NZ,OA,PL,PT,RO,RU,SD,SE,SG,SI,SK,SL,TJ,TM,TR,TT,TZ,UA,UG,UZ,VN,YU,
   The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the *applicant to furnish a copy of the international application (Rule 49.1(a-bis)).*

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on
   05 April 2001 (05.04.01) under No. WO 01/23336

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a **demand for international preliminary examination** must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the **national phase**, he must, within 20 months *or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.*

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer
J. Zahra

Telephone No. (41-22) 338.83.38

Ing. B. & Z. MILANO
17 APR 2001

3929617

heat equal to 28 Kcal/moles of styrene corresponding to 270 Kcal/kg of styrene produced.

The high heat required and the high thermal levels at which it must be exchanged greatly influence the technological design.

The technologies at present commercialized (Fina/Badger and Lummus/UOP Classic SM processes) satisfy the demands imposed by the thermodynamics of the reaction by means of processes which use a bulk catalyst prevalently based on iron oxide and promoted with alkalis, and which comprise the use of:

- several adiabatic reactors in series, with intermediate heating steps at a temperature ranging from 540°C to 630°C and with contact times in the order of tenths of a second;
- radial flow reactors which operate under vacuum at a pressure ranging from 0.3 to 0.5 ata (absolute atmospheres); and
- water vapor which is fed with the charge to be dehydrogenated.

Water is the main component in the charge fed to the reactor. The typical molar concentration is 90%, even if higher concentrations are often adopted to lengthen the chemical life of the catalyst.

The vapor has the function of:

por heat and not that of the latent heat;

- carrying out the reaction under vacuum (average absolute pressure of 0.4 ata) and therefore in extremely diluted phase in EB; the partial EB pressure is on an average equal to 0.04 ata.

It has now been found that it is possible to overcome these drawbacks by means of a process which uses a fluid-bed reactor/regenerator system and a catalyst based on iron oxide supported on a microspheroidal alumina modified with silica and further metal oxides as promoters.

The process of the present invention has considerable economic advantages, in particular:

- thermal profile of the reactor favorable for the reaction thermodynamics;

- the heat is directly transferred to the reaction by the regenerated catalyst, superheating ovens are therefore not required for the thermal exchange and the strong remixing of the fluidized bed prevents the formation of hot spots which would lower the selectivity;

- the possibility of recycling the hydrogen;

- the plant can be run with great flexibility in terms of actual productive capacity with respect to that projected;

- the dehydrogenation reaction and the regeneration take

cantly the catalytic performances in dehydrogenation yield, with evident advantages. In the same time, the mechanical resistance of the catalyst itself is improved by silica modification making it more suited to fluid bed operations. Furthermore, the catalyst is also able to operate with nitrogen other than with water.

In accordance with this, the present invention relates to a process for dehydrogenating ethylbenzene to styrene which essentially consists in:

(a) reacting ethylbenzene mixed with an inert product, in a fluid-bed reactor, in the presence of a catalytic system consisting of iron oxide and promoters supported on alumina modified with 0.01-10% by weight of silica and operating at a temperature ranging from 400 to 700°C, at a total pressure of 0.1 to 3 ata and with a GHSV space velocity ranging from 50 to 10,000 h^{-1} (normal liters of the mixture ethylbenzene and inert gas/h x liter of catalyst); and

(b) regenerating the catalyst in a regenerator by burning the coke deposited on its surface at a temperature exceeding 400°C.

The catalytic system used in the process of the present invention consists of:

(1) 1-60% by weight, preferably 1-20%, of iron oxide;

(2) 0.1-20% by weight, preferably 0.5-10%, of at least

of the promoters on the modified carrier (a);

(d) drying at 100-150°C and calcination of the dried solid at a temperature ranging from 500 to 900°C.

Steps c) and d) can be repeated several times.

Nitrogen, methane, hydrogen or water vapor can be used as the gaseous inert product, in a volumetric ratio inert gas/ethylbenzene ranging from 1 to 6, preferably from 2 to 4. Methane and nitrogen are preferably used.

According to a further embodiment of the process of the present invention, the ethylbenzene can be co-fed to the reactor with a paraffin selected from ethane, propane, isobutane, in order to obtain the contemporaneous dehydrogenation of the co-fed products to give styrene and the corresponding olefins respectively.

In particular when the ethylbenzene is fed with ethane, the process can be carried out as described in U.S. patent 6,031,143.

In the reactor-regenerator system, the catalyst circulates continuously, in fluidized state, between the reactor and regenerator, thus allowing the process to be carried out in continuous.

The heat necessary for the reaction is provided by the regenerated catalyst which reaches the reactor at a temperature higher than the average reaction temperature.

the regenerated catalyst; there is therefore no need for super-heating ovens for the thermal exchange and the strong re-mixing of the fluid bed prevents the formation of hot spots which would lower the selectivity;

- the hydrogen can be recycled;
- the process can be carried out in continuous without having to modify the operating parameters during the life of the plant;
- the reaction and regeneration take place in physically separated zones so that the hydrocarbon streams do not mix with streams containing oxygen;
- the molar concentration inert product/ethylbenzene in the feeding is much lower with respect to the commercial technologies.

With reference to figure 1, a possible application of the reactor-regenerator scheme is provided, which uses the catalyst based on supported iron oxide.

The liquid stream of ethylbenzene (1), consisting of fresh and recycled feeding, at room temperature and a pressure of 2.6 ata, is vaporized in the evaporator (2), preheated to about 420°C in the gas-gas exchanger (3), mixed in a suitable mixer (4) with a stream (5) prevalently consisting of nitrogen and whose origin is described hereunder, and fed to the reactor (6) by means of an appropriate distributor situated in the lower

The resulting stream (5) is then treated as described above.

All the catalytic tests are carried out using a quartz micro-reactor in which about 50-100 ml of catalyst are charged. The reactor is heated by an electric oven in order to keep the catalytic bed at the desired temperature.

The ethylbenzene is fed to an evaporator by means of a dosing pump and is then mixed with the inert gas whose flow-rate is measured by means of a rotameter.

The reaction mixture is preheated to 200°C and fed to the reactor from below through a calibrated septum which acts as gas distributor, thus fluidizing the catalyst.

A quartz expansion vase is assembled on the head of the reactor, which has the function of decelerating the effluent gas and making the fine catalyst particles fall back into the reactor. The expander and sampling lines are maintained at 200°C to avoid the condensation of styrene, non-reacted ethylbenzene and any possible heavy by-products.

The catalytic cycle consists of:

- a reaction phase, in which the ethylbenzene mixed with the inert product or with the paraffin, is fed to the reactor over a period of 10 minutes;

part. The stream (7), effluent from the reactor at a temperature of 600°C, at a pressure of 1.34 ata, essentially consisting of nitrogen, styrene, hydrogen and non-reacted ethylbenzene, undergoes a first cooling in the gas-gas exchanger (3) and a second cooling in the gas-gas exchanger (8), from which it flows at a temperature of 320°C. This stream then passes through the filter system (9) to eliminate the fine particles entrained and is subsequently cooled with water to a temperature of 40°C in the exchanger (10). The mixture becomes biphasic at this temperature as a result of the partial condensation of the hydrocarbon.

The condensed stream (12) is recovered from the bottom in the phase separator (11), and is sent, like the gas stream (13), to the subsequent recovery and purification zone of the products (14), not shown in detail, where the following streams are recovered, using techniques known to experts in the field:

- stream (15) consisting of pure styrene (product);
- stream (16) consisting of ethylbenzene, which is recycled to the dehydrogenation;
- stream (17) essentially consisting of nitrogen and hydrogen, containing light hydrocarbons;
- stream (18) essentially consisting of benzene and toluene;

- stream (19) consisting of heavy hydrocarbon by-products.

The stream (17), after flushing stream (20), is heated in the gas-gas exchanger (21) up to a temperature of about 550°C and fed to the regenerator (22) by means of the distributor (23) situated above the air inlet. The stream of air (24) is compressed in the compressor (25) and preheated to a temperature of 560°C in the gas-gas exchanger (26), before being fed to the regenerator (22). The stream (27) effluent from the regenerator, prevalently consisting of nitrogen and water vapor is subsequently cooled in the exchangers (21) and (26), passes through the filters (28) to eliminate the fine powders entrained and is cooled in the exchanger (29) at 40°C.

The stream of condensed water (30) is separated in the vessel (31), whereas the remaining gas stream (32), still containing significant quantities of water vapor, is compressed in the compressor (33) at a pressure of 2.6 ata and is subsequently cooled in the exchanger (34) at such a temperature as to allow the almost complete condensation of the water present. The condensed stream (35) is removed from the bottom of the vessel (36), whereas the gas stream (37), after a part of it has been flushed (38), is heated in the gas-gas exchanger (8).

TABLE I

				Feeding					Conversion	Selectivity	Styrene yield
Ex.	Fe_2O_3%	K_2O%	T°C	EB%vol	H_2O%vol	N_2%vol	P ata	pEB	Ethylbenzene %	Styrene mol.%	mol.%
1	6.6	4	540	20	0	80	1.1	0.22	50	93	47
1 bis	6.6	4	540	20	60	20	1.1	0.22	42	96	40
1 ter	6.6	4	572	20	60	20	1.1	0.22	53	87	46
2	6.6	4	545	20	0	80	1.1	0.22	50	89	45
2 bis	6.6	4	570	20	60	20	1.1	0.22	52	85	44
3	6.6	1.9	550	20	0	80	1.1	0.22	50	87	44
3 bis	6.6	1.9	580	20	60	20	1.1	0.22	50	84	42
4	6.5	0.8	580	20	0	80	1.1	0.22	50	82	41
4 bis	6.5	0.8	580	20	17	63	1.1	0.22	31	79	24
5	10.4	4	550	20	0	80	1.1	0.22	50	87	44
5 bis	10.4	4	572	20	60	20	1.1	0.22	51	84	43

Examples 1bis-5bis are comparative examples carried out in the presence of water

TABLE 2

Ex.	Catalyst composition (%)						Feed (%V)				Conv. EB %	Select. Styrene % mol	Yield Styrene % mol
	Fe_2O_3	K_2O	Ce_2O_3	La_2O_3	T°C	HOS	EB	H_2O	N_2	P ata			
6	5.0	3.6	0.5	0.5	560	30	20	0	80	1.1	56.2	82.7	46.5
6					560	150	20	0	80	1.1	57.3	86.9	49.8
7	5.0	3.6	0.5	0.5	560	34	20	0	80	1.1	57.9	73.5	42.6
7					580	59	20	0	80	1.1	64.8	56.1	36.4
7					560	188	20	0	80	1.1	56.9	77.9	44.3

TABLE 3

Feeding			Pressure ata	PEB	pEthane	Conversion		Selectivity	
EB % vol.	Ethane % vol.	H_2O				EB %	Ethane %	Styrene mol. %	Ethylene mol. %
10	90	0	1.1	0.11	0.99	59	13	90	90
20	80	0	1.1	0.22	0.88	53	10	92	93
30	70	0	1.1	0.33	0.77	45	8	94	93

Claims

1. A process for the dehydrogenation of ethylbenzene to styrene which comprises:

(a) reacting the ethylbenzene mixed with an inert gas in a fluid-bed reactor, in the presence of a catalytic system consisting of iron oxide and promoters supported on alumina modified with 0.01-10% by weight of silica and operating at a temperature ranging from 400 to 700°C, at a total pressure of 0.1 to 3 ata and with a GHSV space velocity ranging from 50 to 10,000 h^{-1} (normal liters of a mixture of ethylbenzene and inert gas/h x liter of catalyst); and

(b) regenerating and heating the catalyst in a regenerator at a temperature exceeding 400°C.

2. The process according to claim 1, wherein the catalyst consists of:

(1) 1-60% by weight of iron oxide;

(2) 0.1-20% by weight of at least one alkaline or alkaline earth metal oxide;

(3) 0-15% by weight of a second promoter consisting of at least one rare earth oxide;

(4) the complement to 100 being a carrier consisting of a microspheroidal alumina selected from those in delta, theta phase or their mixtures, in

isobutene obtaining the contemporaneous dehydrogenation of the components of the mixture to give styrene and the corresponding olefins, respectively.

17. The process according to claim 16, wherein the ethylbenzene is fed to the reactor mixed with ethane obtaining the contemporaneous dehydrogenation of the components of the mixture to give styrene and ethylene respectively.

18. The process according to claim 17, wherein the ethylene is recycled to an alkylation unit together with a stream of benzene to give ethylbenzene.